DISTRIBUTION OF MATTER IN THE SEA AND ATMOSPHERE

Changes in the Carbon Dioxide Content of the Atmosphere and Sea due to Fossil Fuel Combustion[1]

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Abstract

The dissociation equilibrium of carbon dioxide in the sea is discussed with particular emphasis on the buffering effect of sea water, when changes of the partial pressure of CO_2 in the gas phase take place. The results are used in a study of the changes of the carbon dioxide content of the atmosphere and the sea that occur as a result of release of CO_2 to the atmosphere by fossil fuel combustion. It is shown that the steady state considerations given by previous authors hereby are considerably modified. Thus an increase of the CO_2 content of the atmosphere of about 10 % as reported by Callendar may be compatible with a Süess effect of only a few percent. Because of the small buffering effect of the sea it seems likely that the biosphere on land may play a more important role for the changes actually occurring in the atmosphere due to release of CO_2 by combustion than previously believed. This problem warrants further investigation, but already the present treatment indicates that an appreciable increase of the amount of CO_2 in the atmosphere may have occurred since last century. This increase will continue and should be detectable with present techniques for measuring CO_2 in the atmosphere within a few years in areas with little or no local pollution due to fossil fuel combustion as in the Antarctica or on Hawaii.

1. Introduction

Fossil fuel combustion has added considerable amounts of carbon dioxide to the atmosphere during the last 100 years. In view of the great importance of CO_2 in the atmosphere for maintaining a radiational balance between the earth and space it is of great interest to know whether this output of CO_2 has caused a significant increase of the total content of carbon dioxide in the atmosphere or whether most of it has been transferred into the oceans. Some twenty years ago CALLENDAR (1938) could show that most likely a noticeable increase of the CO_2 in the atmosphere had occurred and he has recently (CALLENDAR, 1958) indicated that this increase

in 1955—56 amounted to about 10 % as compared with an output due to combustion of about 14 % of the total amount of CO_2 present in the atmosphere (cf. REVELLE and SÜESS, 1957). His conclusions have recently been supported by BRAY (1959) in a detailed statistical investigation. However, by studying the C^{14} distribution in the atmosphere and the sea and its variation in the atmosphere during the last 100 years as revealed by the ratio C^{14}/C^{12} in wood one has been able to show that the exchange time between the atmosphere and the ocean is about 5 years (CRAIG, 1957, 1958; REVELLE and SÜESS, 1957; ARNOLD and ANDERSON, 1957; RAFTER and FERGUSSON, 1958). It has then been concluded (REVELLE and SÜESS, l.c.) that most of the CO_2 due to combustion has been transferred into the ocean and that a net increase of CO_2 in the atmosphere of only

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a few percent has actually occurred. Callendar's deduction has therefore been rejected particularly since the CO_2 measurements from the 19th century are indeed very uncertain.

Towards the end of their paper Revelle and Süess point out, however, that the sea has a buffer mechanism acting in such a way that a 10 % increase of the CO_2-content of the atmosphere need merely be balanced by an increase of about 1 % of the total CO_2 content in sea water to reach a new equilibrium. The crude model of the sea they used assuming it to be one well-mixed reservoir of CO_2, did not permit them to study the effect of this process more in detail.

The low buffering capacity of the sea mentioned by Revelle and Süess is due to a change in the dissociation equilibrium between CO_2 and H_2CO_3 on one hand and HCO_3 and CO_3 ions on the other. An addition of CO_2 to the water will change the pH and thereby decrease the dissociation resulting in a larger portion of CO_2 and H_2CO_3 molecules. Since the pressure of CO_2 in the gas phase being in equilibrium with CO_2 dissolved in water is proportional to the number of CO_2 and H_2CO_3 molecules in the water, an increase of the partial pressure occurs which is much larger (about 12.5 times) than the increase of the *total content* of CO_2 in the water. The change of this equilibrium in the sea is almost instantaneous. However, in course of its circulation the ocean water gets in contact with solid $CaCO_3$ on the bottom of the sea whereby a change towards another equilibrium takes place. This latter process is extremely slow and may be disregarded when discussing changes due to fossil fuel combustion. It will, however, be indicated in section 2 how this equilibrium is of major interest when being concerned with processes with a time scale of several thousand years.

In discussing the consequences of such a shift in the dissociation equilibrium with respect to the exchange of CO_2 between the atmosphere and the sea and within the sea it is not sufficient to treat the ocean as one well-mixed reservoir. We shall instead first follow a suggestion by CRAIG (1957) and divide the ocean in two layers. The upper reservoir, in direct contact with the atmosphere, is the part of the ocean located above the thermocline and constitutes about 1/50 of the total sea. This part of the ocean is well mixed due to wind action and convection. The remaining part of the ocean, the deep sea,

is also taken as a well-mixed water body in direct exchange with the mixed layer above. Certainly this latter assumption is a poor approximation to actual conditions but will, as we shall see, give internally consistant results. In the first instance we shall neglect the effect of living matter on the earth but some general remarks about the exchange of CO_2 between vegetation and the atmosphere will be given towards the end of the paper.

It is obvious that an addition of CO_2 to the atmosphere will only slightly change the CO_2 content of the sea but appreciably effect the CO_2 content of the atmosphere. It is possible to deduce a relation between the exchange coefficient for transfer from the atmosphere to the sea and the corresponding coefficient for the exchange between the deep sea and the mixed layer. It turns out that a 10 % increase of the CO_2 content of the atmosphere as a result of a total output due to combustion amounting to 13 % of the total CO_2 content of the atmosphere would result for a residence time of water in the deep sea of around 500 years. Only a considerably more rapid turn over of the ocean model yield appreciably lower values, while the rate of exchange between the atmosphere and the sea is much less important.

The change in the dissociation equilibrium in water resulting from a transfer of CO_2 to the sea also effects the C^{14} distribution in the three reservoirs and REVELLE's and SÜESS' (1957) considerations in this matter are thereby appreciably changed. It is clear that a large percentage change of the CO_2 in the atmosphere and a comparatively small percentage change in the sea will yield a C^{14}/C^{12} ratio in the sea which is considerably greater than that of the atmosphere. The distribution of C^{14} between these two reservoirs is therefore not in equilibrium any longer. A transfer of C^{14} from the sea to the atmosphere will result. A more detailed study of this secondary effect reveals that

a) the steady state considerations of CO_2 exchange between the atmosphere and the sea as given by CRAIG (1957, 1958) are somewhat modified and a likely residence time for CO_2 in the atmosphere is 5 years.

b) the Süess effect would be 3—5 % depending on the rate of overturning of the sea.

In view of the observed values of the Süess-effect being around 3 % in 1954 (before the hydrogen bomb tests) (cf. BROECKER and WALTON, 1959; DE VRIES, 1958) the values obtained in this

analysis are somewhat too large if using a value for the residence of water in the deep sea of 500 years. One possible explanation of this discrepancy would be the neglect of the exchange of CO_2 between the atmosphere and the biosphere. The main difficulty met when trying to incorporate this effect is, that we actually do not know whether a net increase of the amount of CO_2 present in vegetation may have occurred due to a transfer from the atmosphere or whether the direct influences from man's activities have had an effect in the opposite direction. It is clear, however, that even if no net transfer of CO_2 from the atmosphere into living or dead matter on land has occurred these exchange processes will modify the estimate of the "Süess effect" obtained by merely considering the atmosphere and the sea.

2. The CO_2-system in the sea

The different components of CO_2 present in the sea are CO_2, H_2CO_3, HCO_3^- and CO_3^{-2}. As CO_2 is difficult to distinguish from H_2CO_3 it is customary to express the sum of these species as CO_2. The sea is also in contact with ample amounts of solid $CaCO_3$ which should be considered in equilibrium being attained over several "turnover times" of the sea itself. Another important item in the system is the carbonate alkalinity, denoted here by A which is the sum of those cations which balance the charges of HCO_3^- and CO_3^{-2}. The following average values for the concentrations of the different components will be used here:

C_{CO_2} = 0.0133 mmol × 1⁻¹ (sum of CO_2 and H_2CO_3)
$C_{HCO_3^-}$ = 1.90 mmol × 1⁻¹
$C_{CO_3^{-2}}$ = 0.235 mmol × 1⁻¹

The sum of all these species is denoted by ΣC_{CO_2} and becomes 2.148 mmol × 1⁻¹. A is given in mval × 1⁻¹ and becomes, $A = C_{HCO_3^-} + 2 C_{CO_3^{-2}} = 2.37$ mval × 1⁻¹. Now the following relationships can be derived, namely

$$\Sigma C_{CO_2} = \left(1 + \frac{K_1}{C_{H^+}} + \frac{K_1 K_2}{C_{H^+}^2}\right) C_{CO_2} \quad (1)$$

$$A = \left(\frac{K_1}{C_{H^+}} + \frac{2K_1 K_2}{C_{H^+}^2}\right) C_{CO_2} \quad (2)$$

where K_1 and K_2 are the first and second dissociation constants of H_2CO_3 in sea water and C_{H^+} is the hydrogen ion concentration. It is convenient to have the average values of the fractions within the brackets. They are

$$\frac{K_1}{C_{H^+}} = 143 \qquad \frac{K_1 K_2}{C_{H^+}^2} = 18$$

As to calcium carbonate, its solubility product L_p can be written

$$C_{Ca^{+2}} \cdot C_{CO_3^{-2}} = L_p$$

or more conveniently

$$C_{Ca^{+2}} = L_p \frac{C_{H^+}^2}{K_1 K_2} \frac{1}{C_{CO_2}} \quad (3)$$

and in sea water $C_{Ca^{2+}} = 10$ mmol × 1⁻¹.

Finally we have for the equilibrium between the atmospheric CO_2 and that in sea water

$$P_{CO_2} = \frac{1}{\alpha} C_{CO_2} \quad (4)$$

where α is a proportionality constant and P_{CO_2} is the partial pressure of CO_2 in the atmosphere.

The constants K_1, K_2, L_p and α are only functions of temperature and salinity and will be regarded as constants in the following. We may therefore consider relations between small variations in P_{CO_2}, C_{CO_2}, ΣC_{CO_2}, A, C_{H^+} and $C_{Ca^{2+}}$. Using the variational method applied on equations (1) to (4) one obtains

$$\frac{\delta \Sigma C_{CO_2}}{\Sigma C_{CO_2}} = \frac{\delta C_{CO_2}}{C_{CO_2}} +$$

$$+ \frac{\frac{\partial}{\partial C_{H^+}}\left(1 + \frac{K_1}{C_{H^+}} + \frac{K_1 K_2}{C_{H^+}^2}\right)}{1 + \frac{K_1}{C_{H^+}} + \frac{K_1 K_2}{C_{H^+}^2}} \delta C_{H^+} \quad (5)$$

$$\frac{\delta A}{A} = \frac{\delta C_{CO_2}}{C_{CO_2}} + \frac{\frac{\partial}{\partial C_{H^+}}\left(\frac{K_1}{C_{H^+}} + \frac{2 K_1 K_2}{C_{H^+}^2}\right)}{\frac{K_1}{C_{H^+}} + \frac{2 K_1 K_2}{C_{H^+}^2}} \delta C_{H^+} \quad (6)$$

$$\frac{\delta C_{Ca^{+2}}}{C_{Ca^{+2}}} = \frac{2 \delta C_{H^+}}{C_{H^+}} - \frac{\delta C_{CO_2}}{C_{CO_2}} \quad (7)$$

$$\frac{\delta P_{CO_2}}{P_{CO_2}} = \frac{\delta C_{CO_2}}{C_{CO_2}} \quad (8)$$

First we see that if P_{CO_2} varies and the hydrogen ion concentration were kept constant, the relative changes would be the same in the sea as in the atmosphere. As the total amount of CO_2 in the sea is about 50 times that in the air, practically all excess CO_2 delivered to the atmosphere would be taken up by the sea when equilibrium has been established. One cannot, however, assume that pH is uninfluenced by changes in the ΣC_{CO_2} of the sea. We may see if any condition can be imposed upon the alkalinity. Obviously this should be kept constant if we consider changes that takes place over a relatively short time interval, less than the "turnover time" of the sea, because A is really the concentration of cations that balance the charges of HCO_3^- and CO_3^{-2}. If $CaCO_3$ is excluded the sum of these charges must remain constant. And then we see that any change in the P_{CO_2} will also change C_{H^+}. From eq. (5), (6) and (8) we get by putting $\delta A = 0$

$$\frac{\delta P_{CO_2}}{P_{CO_2}} = \frac{\delta C_{CO_2}}{C_{CO_2}} = 12.5 \frac{\delta \Sigma C_{CO_2}}{\Sigma C_{CO_2}} \qquad (9)$$

using the numerical values listed earlier. This tells us that 1 percent change in the total CO_2 concentration in the sea would require 12.5 percent change in the atmospheric CO_2 to maintain equilibrium. If we consider only the "mixed layer" of the oceans, i.e. the surface layer which contains about as much CO_2 as the atmosphere less than 10 percent of the excess fossil CO_2 in the atmosphere should have been taken up by the mixed layer. It is therefore obvious that the mixed layer acts as a bottleneck in the transport of fossil CO_2 into the deep sea (cf. the following section).

It may be of interest also to consider the effect of the $CaCO_3$ on the bottom of the oceans; the effect this may have for the final equilibrium which is attained after a long time. Then alkalinity will change by $\delta A = 2 \ \delta C_{Ca^{+2}}$ and with this condition using the whole system of equations and $C_{Ca^{+2}} = 10$ mmol $\times 1^{-1}$,

$$\frac{\delta P_{CO_2}}{P_{CO_2}} = \frac{\delta C_{CO_2}}{C_{CO_2}} = 2.36 \frac{\delta \Sigma C_{CO_2}}{\Sigma C_{CO_2}} \qquad (10)$$

which shows that the sea, given enough time, has an appreciable buffer capacity for atmospheric CO_2. However, in the case of eq. (10) part of the change of total CO_2 comes from dissolution or precipitation of $CaCO_3$ and this has obviously to be subtracted if we want to know how much of the excess of atmospheric CO_2 the sea ultimately can consume. The amount that dissolves or precipitates is obviously equal to $\delta C_{Ca^{+2}}$ and becomes

$$\delta C_{Ca^{+2}} = 0.444 \frac{\delta C_{CO_2}}{C_{CO_2}}$$

Expressed as a part of the total CO_2 it becomes

$$\frac{\delta C_{Ca^{+2}}}{\Sigma C_{CO_2}} = 0.206 \frac{\delta C_{CO_2}}{C_{CO_2}} \qquad (11)$$

Now, rewriting (9) we find

$$\frac{\delta \Sigma C_{CO_2}}{\Sigma C_{CO_2}} = 0.424 \frac{\delta C_{CO_2}}{C_{CO_2}}$$

The part of the increase in total CO_2 that has come from the atmosphere is therefore

$$\Delta \frac{\delta \Sigma C_{CO_2}}{\Sigma C_{CO_2}} = \frac{\delta \Sigma C_{CO_2}}{\Sigma C_{CO_2}} - \frac{\delta C_{Ca^{+2}}}{\Sigma C_{CO_2}} = 0.238 \frac{\delta C_{CO_2}}{C_{CO_2}} \qquad (12)$$

or

$$\frac{\delta P_{CO_2}}{P_{CO_2}} = \frac{\delta C_{CO_2}}{C_{CO_2}} = 4.20 \Delta \left(\frac{\delta \Sigma C_{CO_2}}{\Sigma C_{CO_2}} \right) \qquad (13)$$

Thus, in equilibrium one percent increase in ΣC_{CO_2} obtained from the atmosphere would occur for a 4.2 percent increase in the atmospheric partial pressure of CO_2. In other words, any excess CO_2 put into the atmosphere will ultimately be distributed so that about $^{11}/_{12}$ of it goes into the sea (again assuming the sea contains, 50 times more CO_2 than the atmosphere) while about $^1/_{12}$ remains in the atmosphere. Of the part that goes into the sea, 87 percent has taken part in the reaction

$$CaCO_3(s) + H_2CO_3(aq) = Ca^{+2} + 2\,HCO_3^{-1}$$
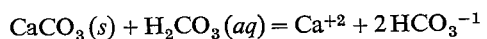
The rest has been used to lower the pH of sea water by the reaction

$$H_2CO_3(aq) \rightarrow H^+ + HCO_3^-$$
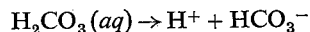
If the turnover time of the sea is of the order of 1,000 years, several thousands of years would be required to reach equilibrium with the $CaCO_3$ at the bottom of the sea.

It should finally be noted that, in case atmospheric CO_2 was withdrawn by some process, this would result in precipitation of $CaCO_3$ in the sea.

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3. The exchange of inactive carbon between the atmosphere and the sea

In order to see more clearly the effect of the shift in the dissociation equilibrium in the sea we shall first disregard the role played by the biosphere and merely consider the atmosphere and the sea, the latter composed of two reservoirs. The top one, the mixed layer, is confined to the layer above the thermocline and the lower one, the deep sea, consists of the remainder of the sea. Both these reservoirs as well as the atmosphere are considered to be well-mixed and the exchange between them takes place through first order exchange processes. Introduce the following notations:

N_i = the total amount of C^{12} and C^{13} in reservoir i in a state of equilibrium as before 1850.

N_i^* = the total amount of C^{14} in reservoir i in a state of equilibrium as before 1850.

N_i' = the amount of C^{12} and C^{13} in reservoir i present in the form of CO_2 or non-dissociated H_2CO_3 (only for the ocean) in a state of equilibrium as before 1850.

$N_i^{*'}$ = the amount of C^{14} in reservoir i present in the form of CO_2 or non-dissociated H_2CO_3 (only for the ocean) in a state of equilibrium as before 1850.

n^i, n_i^*, n_i', $n_i^{*'}$ indicate the deviations from the equilibrium values given above.

k_{i-j} = exchange coefficient for transfer of C^{12} and C^{13} from reservoir i to reservoir j.

k_{i-j}^* = exchange coefficient for transfer of C^{14} from reservoir i to reservoir j.

$\tau_{i-j} = 1/k_{i-j}$

$\tau_{i-j}^* = 1/k_{i-j}^*$

λ = decay constant for C^{14}

$\gamma(t)$ = release of C^{12} and C^{13} due to fossil fuel combustion as a function of time t.

Q = mean production of C^{14} in the atmosphere due to cosmic rays.

The indices a, m and d refer to the atmosphere, the mixed layer and the deep sea respectively. The nomenclature is in part very similar to that used by CRAIG (1957).

Considering now first conditions for inactive carbon we obtain the following equilibria

$$\left. \begin{aligned} -k_{a-m}N_a + k_{m-a}N_m' &= 0 \\ k_{a-m}N_a - k_{m-a}N_m' - k_{m-d}N_m + k_{d-m}N_d &= 0 \\ k_{m-d}N_m - k_{d-m}N_d &= 0 \end{aligned} \right\} \tag{14}$$

Notice here particularly that the transfer from the sea to the atmosphere is put proportional to N_m' and not to the total amount of carbon in the mixed layer, N_m. On the other hand the transfer from the mixed layer to the deep sea and *vice versa* is due to the motion of water and should therefore be proportional to the total amounts of carbon present in the two reservoirs, *i.e.* N_m and N_d respectively. It should be pointed out here that an exchange of carbon between various strata of the ocean also occurs through the motion of organisms and the settling of dead organic material and precipitated $CaCO_3$ which is gradually being dissolved. From a recent paper by ERIKSSON (1958) it can be estimated that this is about 1/3,000 of the total amount of CO_2 in the sea per year. Naturally it is compensated by an upward flux of dissolved CO_2. This flux is small compared to the advective flux from deep water which is about the same as the horizontal transfer of atmospheric CO_2 in Eriksson's model giving a residence time of ≈ 600 years. His paper suggests anyway that the ratio between advective flux and gravitational is about 5. From (14) we now get

$$\left. \begin{aligned} k_{m-a} &= \frac{N_a}{N_m'} k_{a-m} = \alpha k_{a-m} \\ k_{m-d} &= \frac{N_d}{N_m} k_{d-m} = \beta k_{d-m} \end{aligned} \right\} \tag{15}$$

Due to combustion a deviation from this equilibrium now has occurred, which is governed by the following set of equations

$$\left. \begin{aligned} \frac{dn_a}{dt} &= -k_{a-m}n_a + k_{m-a}n_m' + \gamma(t) \\ \frac{dn_m}{dt} &= k_{a-m}n_a - k_{m-a}n_m' - k_{m-d}n_m + k_{d-m}n_d \\ \frac{dn_d}{dt} &= k_{m-d}n_m - k_{d-m}n_d \end{aligned} \right\} \tag{16}$$

In the previous section we found that the following relation exists between n_m' and n_m (cf. eq. (9))

$$n_m' = 12.5 \frac{N_m'}{N_m} n_m = B_1 n_m \tag{}$$

Introducing this expression for n_m' into (16) we obtain a system of three ordinary linear differential

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equations for the three dependant variables n_a, n_m and n_d. Eliminating two of the three variables we obtain

$$\frac{d^3 n_i}{dt^3} + [(1 + B_1\alpha)k_{a-m} + (1 + \beta)k_{d-m}]\frac{d^2 n_i}{dt^2} +$$

$$+ [1 + B_1\alpha + \beta]k_{a-m}k_{d-m}\frac{dn_i}{dt} = S_i \quad (18)$$

$$i = a, m, d$$

where

$$S_a = \gamma''(t) + [B_1\alpha k_{a-m} + (1 + \beta)k_{d-m}]\gamma'(t) +$$
$$+ B_1\alpha k_{a-m}k_{d-m}\gamma(t)$$
$$S_m = k_{a-m}\gamma'(t) + k_{a-m}k_{d-m}\gamma(t) \qquad (19)$$
$$S_d = \beta k_{a-m}k_{d-m}\gamma(t)$$

The general solution of (18) is

$$n_i = C_{1i}e^{\lambda_1 t} + C_{2i}e^{\lambda_2 t} + C_{3i}e^{\lambda_3 t} + P_i \quad (20)$$

where C_{1i}, C_{2i} and C_{3i} are integration constants, λ_1, λ_2 and λ_3 solutions to the algebraic equation

$$\lambda_3 + [(1 + B_1\alpha)k_{a-m} + (1 + \beta)k_{d-m}]\lambda^2 +$$

$$+ [1 + B_1\alpha + \beta]k_{a-m}k_{d-m}\lambda = 0 \quad (21)$$

and P_i are particular solutions depending on the functions S_i. Assuming now that [CRAIG (1957)]

$$N_m = 1.2 \, N_a$$
$$N_d = 60 \, N_a \qquad (22)$$

we obtain

$$B_1\alpha = 12.5 \frac{N_m'}{N_m} \frac{N_a}{N_m'} = 10.4$$
$$\beta = \frac{N_d}{N_m} = 50 \qquad (23)$$

The values chosen for N_m and N_d are somewhat uncertain but as we shall see later, do not influence the results significantly. The solutions to eq. (21) then are, due regard taken to the fact that $k_{a-m} \gg \gg k_{d-m}$ and thus $(1 + B_1\alpha) \cdot k_{a-m} + (1 + \beta)k_{d-m} \gg \gg (1 + B_1\alpha + \beta)k_{a-m}k_{d-m}$ where $\gg$ denotes about two orders of magnitude

$$\lambda_1 = 0$$
$$\lambda_2 = -\frac{(1 + B_1\alpha + \beta)k_{a-m}k_{d-m}}{(1 + B_1\alpha)k_{a-m} + (1 + \beta)k_{d-m}} \qquad (24)$$
$$\lambda_3 = -[(1 + B_1\alpha)k_{a-m} + (1 + \beta)k_{d-m}]$$

To obtain the particular solutions we have to specify $\gamma(t)$. We shall assume that $\gamma(t)$ may be approximated by

$$\gamma(t) = \gamma_0 e^{rt} \qquad (25)$$

where

$$\gamma_0 = 4.96 \, N_a \, 10^{-4}$$
$$r = 0.029 \text{ year}^{-1} \qquad (26)$$

which fits the values given by REVELLE and SÜESS (1957) for carbon production until today and also the estimated values to year 2010 with sufficient accuracy if $t = 0$ at 1880 (see table 1).

Table 1. CO_2 added to the atmosphere by fossil fuel combustion and a comparison with an analytical expression

Decade	Average amount added per decate (% of N_a)		Cumulative total added (% of N_a)	
	measured or estimated	$\gamma(t)$	measured or estimated (since 1860)	$\int_0^t \gamma(t)dt$ (since 1880)
1880—89	0.54	0.57	1.13	0.57
1890—99	0.79	0.77	1.92	1.34
1900—09	1.27	1.03	3.19	2.37
1910—19	1.72	1.37	4.91	3.74
1920—29	2.00	1.83	6.91	5.57
1930—39	2.11	2.47	9.02	8.04
1940—49	2.71	3.17	11.73	11.21
1950—59	3.9	4.4	15.6	15.6
1960—69	5.4	5.8	21.0	21.4
1970—79	7.5	8.0	28.5	29.4
1980—89	10.5	10.4	39.0	39.8
1990—99	14.5	13.7	53.5	53.5
2000—09	20.0	19.0	73.5	72.5

Thus we obtain

$$S_a = \gamma_0[r^2 + \{B_1\alpha k_{a-m} + (1 + \beta)k_{d-m}\}r +$$
$$+ B_1\alpha k_{a-m}k_{d-m}]e^{rt} = \gamma_0 S_{a0}e^{rt}$$
$$S_m = \gamma_0[k_{a-m}r + k_{a-m}k_{d-m}]e^{rt} = \gamma_0 S_{m0}e^{rt} \quad (27)$$
$$S_d = \gamma_0\beta k_{a-m}k_{d-m}e^{rt} = \gamma_0 S_{d0}e^{rt}$$

One then easily finds the particular solutions

$$P_i = \frac{\gamma_0}{r} \frac{S_{i0}}{S_{a0} + S_{m0} + S_{d0}}e^{rt} \qquad (28)$$
$$i = a, m, d$$

In order to determine the three constants C_{ij} for each solution $n_i(t)$ we shall apply the initial conditions

$$n_a = n_m = n_d = 0$$

which yields

$$\frac{dn_a}{dt} = \gamma(t); \qquad \frac{dn_m}{dt} = \frac{dn_d}{dt} = 0$$

$$\frac{d^2 n_a}{dt^2} = \gamma'(t) - k_{a-m}\gamma(t) \qquad t = 0$$

$$\frac{d^2 n_m}{dt^2} = k_{a-m}\gamma(t);$$

$$\frac{d^2 n_d}{dt^2} = 0$$

$$\quad (29)$$

These equations are obtained from the system (16) and also yield

$$n_a + n_m + n_d = \frac{\gamma_0}{r}(e^{rt} - 1) \qquad (30)$$

As can easily be verified the final solutions of n_a, n_m and n_d will be independant of the exact initial conditions for $t \gg 200$ years if the values for τ_{a-m} and τ_{d-m} are of the order of 5 and 500 years respectively. It also follows that $\lambda_3 = -2$ years^{-1} and that thus the term containing exp $(\lambda_3 t)$ in (20) may be neglected for $t \gg 2$—3 years. With due regard taken to this latter fact we finally obtain

$$n_a = \frac{\gamma_0}{r}\left[\frac{S_{a0}}{S}(e^{rt} - 1) + \right.$$
$$\left. + \frac{r}{\lambda_2}\left(1 - \frac{S_{a0}}{S}\right)(e^{\lambda_2 t} - 1) \right]$$

$$n_m = \frac{\gamma_0}{r}\frac{S_{m0}}{S}\left[(e^{rt} - 1) - \frac{r}{\lambda_2}(e^{\lambda_2 t} - 1) \right] \quad (31)$$

$$n_d = \frac{\gamma_0}{r}\frac{S_{d0}}{S}\left[(e^{rt} - 1) - \frac{r}{\lambda_2}(e^{\lambda_2 t} - 1) \right]$$

$$S = S_{a0} + S_{m0} + S_{d0}$$

From CRAIG's (1957, 1958) investigation of the exchange time for carbon dioxide between the atmosphere and the sea and the exchange within the sea the best estimates of τ_{a-m} and τ_{d-m} at present are $\tau_{a-m} = 5$ years and $\tau_{d-m} = 500$—1,000 years. FERGUSSON and RAFTER (1958) give a value $\tau_{a-m} = 3$ years. Fig. 1 shows the amount to be expected in the atmosphere 1954, when the total fossil fuel combustion since the middle of the last century is estimated to have been 13.2 % of the previous content of the atmosphere, for values of τ_{a-m} and τ_{d-m} in the vicinity of those quoted above. It first of all shows that
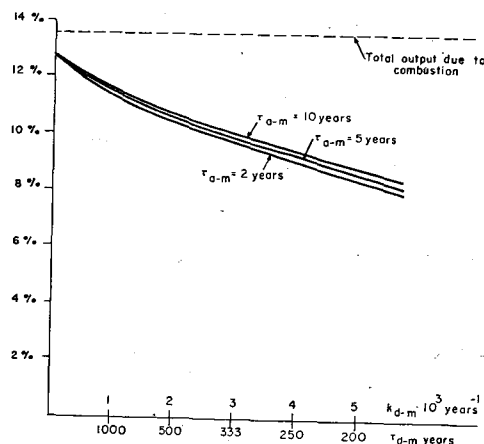

Fig. 1. Net increase of CO_2 in the atmosphere in 1954 due to release of fossil CO_2 according to UN-estimates as dependant on the rate of exchange between the atmosphere and the sea and the mixed layer and the deep sea.

the net increase in the atmosphere is almost independant of the precise rate of exchange between the atmosphere and the sea. This depends on the fact that the top layer of the ocean only need to absorb a small amount of CO_2 from the atmosphere as compared to the quantities released to be in approximate balance. Its capacity is therefore too small to be of any major importance. The decisive factor is instead the rate of overturning of the deep sea. Thus even using a residence time of only 200 years for the deep sea water an 8—9 percent increase of CO_2 in the atmosphere must have taken place. For a value of $\tau_{d-m} = 500$ years an increase of the atmosphere's content of CO_2 of about 10 percent would have occurred in 1954. This value compares very favourably with the value of 10 percent given by CALLENDAR (1958) as the total increase until 1955 deduced from a careful survey of all available measurements.

The results obtained above are, however, dependant on our assumptions of the size of the three reservoirs, i.e. N_a, N_m and N_d. Of course, the total amount of CO_2 in the atmosphere, N_a is quite well known, but the division of the sea into two layers is somewhat arbitrary. It is of some interest to see how sensitive the solution is to a variation of N_m and N_d. Instead of chosin the values given in (22) we shall assume

$$\text{a)} \begin{cases} N_m = 0.8 \ N_a \\ N_d = 60 \ N_a \end{cases} \quad \text{b)} \begin{cases} N_m = 2 \ N_a \\ N_d = 59 \ N_a \end{cases} \quad (32$$

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We then obtain the values $n_a = 10.6\%$ and $n_a = 10.0\%$ respectively as compared with $n_a = 10.3\%$ previously, using $\tau_{a-m} = 5$ years and $\tau_{d-m} = 500$ years. Our solution is quite insensitive to the exact division of the ocean. However, the value of the total amount of carbon dioxide in the sea ($\approx 61\,N_a$) effects the solution more, but here we quite accurately know the actual amounts as just mentioned.

4. The exchange of radio-carbon between the atmosphere and the sea

REVELLE and SÜESS (1957) assume that the exchange of radio carbon between the atmosphere and the sea takes place independantly of changes in the distribution of inactive CO_2. If this were the case the decrease of the C^{14}/C^{12} ratio in the atmosphere since 1850, the Süess effect, would be a direct measure of the increase of the inactive CO_2 during the same time, since fossil fuel contains no C^{14}. As a matter of fact, they deduce an exchange coefficient for transfer of CO_2 from the atmosphere to the sea on this bases. As was indicated in the introduction this is not correct. The change of pH in the sea will shift the dissociation equilibrium also for the carbon dioxide containing C^{14}. We may assume an equilibrium rapidly being established and have

$$\frac{N_m^{*'}}{N_m^*} = \varkappa \frac{N_m'}{N_m} \tag{33}$$

where $\varkappa$ is dependant on the fractionation. If changes of N_m and N_m' occur as discussed in the previous section, we obtain by variation the following expression for the changes in N_m^* and $N_m^{*'}$

$$\frac{n_m^{*'}}{N_m^{*'}} - \frac{n_m^*}{N_m^*} = \frac{n_m'}{N_m'} - \frac{n_m}{N_m} \tag{34}$$

Making use of (17) we obtain

$$\left.\begin{aligned}
n_m^{*'} &= \frac{n_m^*}{N_m^*} N_m^{*'} + 11.5 \frac{n_m}{N_m} N_m^{*'} \\
&= B_2 n_m^* + B_3 n_m
\end{aligned}\right\} \tag{35}$$

We see here clearly how a change of the total amount of CO_2 in the top layer of the ocean will influence the amount of radioactive carbon in the form of CO_2 and H_2CO_3 and therefore the partial pressure, which will mean that the equilibrium with the atmosphere is disturbed. Actually the amount of C^{14} in the form of undissociated CO_2 is much more influenced by changes in the *total* amount of CO_2 present in the water than by changes of the amount of *radioactive* carbon dioxide.

Corresponding to the system of equations in (16) we have the following set describing the transfer of radioactive carbon

$$\left.\begin{aligned}
\frac{dn_a^*}{dt} &= - k_{a-m}^* n_a^* + k_{m-a}^* n_m^{*'} \quad - \lambda n_a^* \\
\frac{dn_m^*}{dt} &= \quad k_{a-m}^* n_a^* - k_{m-a}^* n_m^{*'} - \\
& \quad\quad - k_{m-d} n_m^* + k_{d-m} n_d^* - \lambda n_m^* \\
\frac{dn_d^*}{dt} &= \quad\quad k_{m-d} n_m^* - k_{d-m} n_d^* - \lambda n_d^*
\end{aligned}\right\} \tag{36}$$

Notice here that the exchange coefficients between the atmosphere and the sea are different from those used in equation (16) thereby taking into consideration the fractionation effect. Following CRAIG (1957) we have

$$\frac{k_{m-a}^*}{k_{a-m}^*} = \mu \frac{k_{m-a}}{k_{a-m}} = \mu \frac{N_a}{N_m'} \approx \frac{N_a}{N_m'} \tag{37}$$

where $\mu = 1/1.012 = 0.988$. The deviation of μ from unity will be completely irrelevant in the following discussion and we will therefore put $\mu = 1$ as indicated by the last expression in (37). We shall also put $k_{a-m}^* = k_{a-m}$ and thus neglect fractionation. For the exchange between the top layer of the ocean and the deep sea the exchange is the same as for inactive carbon with the assumption made that it is due to the motion of sea water only.

Introducing (35) into (36), taking into consideration (15) and (37) and rearranging terms we obtain

$$\left.\begin{aligned}
\left(\frac{d}{dt} + k_{a-m} + \lambda\right) n_a^* - B_2 \alpha k_{a-m} n_m^* \quad &= B_3 \alpha k_{a-m} n_m \\
- k_{a-m} n_a^* + \left(\frac{d}{dt} + B_2 \alpha k_{a-m} + \beta k_{d-m} + \lambda\right) n_m^* - k_{d-m} n_d^* &= - B_3 \alpha k_{a-m} n_m \\
- \beta k_{d-m} n_m^* + \left(\frac{d}{dt} + k_{d-m} + \lambda\right) n_d^* &= 0
\end{aligned}\right\} \tag{38}$$

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We find thus that the changes of n_m appear as "driving forces" for the C^{14}-system. Knowing n_m as a function of time, we may calculate the changes that will occur in the distribution of radio carbon and thus also compute the Süess effect. The problem is implicit, however, since the distribution of n_m depends on k_{a-m} and k_{d-m} as shown in the previous section and our problem

is therefore to find the particular pair of values that are in agreement with observed changes in the total amount of CO_2 in the atmosphere *and* the changes of the C^{14}/C^{12} ratio. Eliminating n_m^* and n_d^* from the equations (38) and in doing so taking account of the fact that $k_{a-m} \gg k_{d-m} \gg \lambda$ we obtain

$$\frac{d^3 n_a^*}{dt^3} + [(B_2\alpha + 1)k_{a-m} + (\beta+1)k_{d-m}]\frac{d^2 n_a^*}{dt^2} + (1+\beta+B_2\alpha)k_{a-m}k_{d-m}\left(\frac{dn_a^*}{dt} - n_a^*\lambda\right) =$$
$$= B_3\alpha k_{a-m}\left[\frac{d^2 n_m}{dt^2} + (\beta+1)k_{d-m}\left(\frac{dn_m}{dt} + \lambda n_m\right)\right] \qquad (39)$$

Now $|n_m^{-1} dn_m/dt| \gg \lambda$ and we shall also assume that our solution n_a^* satisfies the same relation, which will be verified *a posteriori*. It means that

the decay of C^{14} is unimportant for the discussion of the exchange between the atmosphere and the sea. We thus finally obtain

$$\frac{d^3 n_a^*}{dt^3} + [(B_2\alpha + 1)k_{a-m} + (\beta+1)k_{d-m}]\frac{d^2 n_a^*}{dt^2} + (1+\beta+B_2\alpha)k_{a-m}k_{d-m}\frac{dn_a^*}{dt} =$$
$$= B_3\alpha k_{a-m}\left[\frac{d^2 n_m}{dt^2} + (1+\beta)k_{d-m}\frac{dn_m}{dt}\right] \qquad (40)$$

This equation is principally the same as eq. (18) and thus possesses a solution of the character given by (20) where now λ_1^*, λ_2^* and λ_3^* are solutions of an equation similar to (24). From the three equations (38) and with due regard to the expression for dn_m/dt given by eq. (16) we obtain the initial conditions

$$n_a^* = \frac{dn_a^*}{dt} = \frac{d^2 n_a^*}{dt^2} = 0 \qquad (41)$$

and similar expressions for n_m^* and n_d^* if we wish to study their variations. Introducing the expression for n_m given by equation (31) and solving for n_a^* we obtain with some simplifications similar to those done previously

$$\frac{n_a^*}{N_a^*} = Q_1\left[e^{rt} - 1 - \frac{r}{\lambda_2^*}(e^{\lambda_2^* t} - 1)\right] -$$
$$- Q_2\left[e^{\lambda_2 t} - 1 - \frac{\lambda_2}{\lambda_2^*}(e^{\lambda_2^* t} - 1)\right] \qquad (42)$$

where

$$\left. \begin{array}{l} Q_1 = \dfrac{[r + (1+\beta)k_{d-m}]H}{r[r^2 + \{(B_2\alpha+1)k_{a-m} + (1+\beta)k_{d-m}\}r + (1+\beta+B_2\alpha)k_{a-m}k_{d-m}]} \\[4mm] Q_2 = \dfrac{[(1+\beta)k_{d-m} + \lambda_2]H}{\lambda_2[\lambda_2^2 + \{(B_2\alpha+1)k_{a-m} + (1+\beta)k_{d-m}\}\lambda_2 + (1+\beta+B_2\alpha)k_{a-m}k_{d-m}]} \end{array} \right\} \qquad (43)$$

having introduced the symbol H and λ_2^* according to

$$H = B_3\alpha\frac{\gamma_0}{r}\frac{k_{a-m}^2(r+k_{d-m})r}{r^2 + [(B_1\alpha+1)k_{a-m} + (1+\beta)k_{d-m}]r + (1+\beta+B_1\alpha)k_{a-m}k_{d-m}} \qquad (44)$$
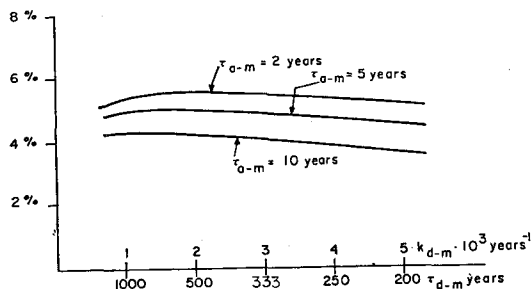
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Fig. 2. The increase of C^{14} in the atmosphere in 1954 by a net transfer from the sea resulting from release of fossil CO_2 and a change of the dissociation equilibrium in the sea.

Fig. 3. The expected value of the Süess effect in 1954 for various rates of exchange between the atmosphere and the sea and within the sea.

$$\lambda_2^* = -\frac{(1 + \beta + B_2\alpha)k_{a-m}k_{d-m}}{(1 + B_2\alpha)k_{a-m} + (1 + \beta)k_{d-m}} \quad (45)$$

Figure 2 shows the values of n_a^* in 1954 when the total output of CO_2 into the atmosphere is estimated to have been 13.2%. A more pronounced variation with the value of $\tau_{a-m} = k_{a-m}^{-1}$ is here obtained than was the case for n_a. This is easily understandable. The slower the exchange between the atmosphere and the sea takes place the less rapid is the response of the sea to changes of the CO_2 content of the atmosphere. If $\tau_{a-m} = 0$ and $\tau_{d-m} = \infty$ obviously $12.5 \times \left(\frac{n_m}{n_a}\right) : \left(\frac{N_m}{N_a}\right) = 1$ according to equation (17). Computing n_m from (31) and inserting we obtain here

$$12.5 \cdot \frac{n_m}{n_a} \cdot \frac{N_a}{N_m} = \begin{cases} 0.77 \\ 0.73 \\ 0.69 \end{cases} \text{ for } \tau_{a-m} \begin{cases} 2 \text{ years} \\ 5 \text{ years} \\ 10 \text{ years} \end{cases} (46)$$

which values are almost independant of the value of τ_{d-m} in the range 200—1,000 years considered here. The changes of n_m are the "driving force" for changes in the C^{14} system and again the slower the exchange between the sea and the atmosphere is, the greater the lag of the C^{14} adjustment in the atmosphere relative to the sea becomes.

The results obtained from eq. (42) are again quite independant of the exact division of the ocean into two reservoirs. Making the computations with the values of N_a and N_m given in (32) yields values of n_a^* only a few tenths of a percent different from those shown in fig. 2.

By a comparison of the results given by eq. (31) and (42) we can compute the changes of the C^{14}/C^{12} ratio in the atmosphere, the "Süess effect". The result is shown in fig. 3. It is of special inte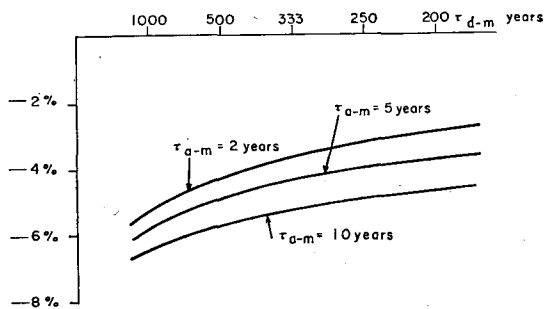rest to compare these values with actually observed values. Süess' measurements give an average value of —1.7% which may be considered representative for about 1946 (REVELLE and SÜESS 1957). BROECKER and WALTON (1959) have found a value of —2.9% for 1938, and a lower value of —1.8% for 1954. The latter sample may, however, already have been influenced by the Castle tests in the Pacific early in 1954. Finally DE VRIES (1958) gives a value of —2.9% for 1954. Summarizing these measurements a value of —2.5 to —3% seems plausible for the Süess effect in 1954 before any appreciable amounts of C^{14} had been introduced into the atmosphere due to atomic bomb tests. More measurements from all over the world would, however, be desirable to determine this value more accurately. It is seen from fig. 3 that the computed value is somewhat larger particularly if the exchange between the three reservoirs is relatively slow.

CRAIG (1958) has given the value $\tau_{a-m} = 5$ years as the most likely value for the exchange time between the atmosphere and the sea. It is obtained by studying the difference in the C^{14}/C^{12} ratio in the atmosphere and the sea with due regard taken to fractionation. It is furthermore assumed that the Süess effect is —1.25%, which seems to be an underestimate even if it is true that some of the values later reported perhaps are not truely representative. Chosing a value of —3% would yield a value of about 3 years. However, due to the fact that a net transfer of CO_2 from the atmosphere to the sea occurs at present $(N_a + n_a)(N_m + n_m)^{-1}$ is somewhat larger than would be the case in equilibrium. On the other hand a net transfer of C^{14} takes place from the sea to the atmosphere and therefore $(N_a^* + n_a^*)(N_m^* + n_m^*)^{-1}$ is smaller than in equilibrium. The deviations are larger the slower the
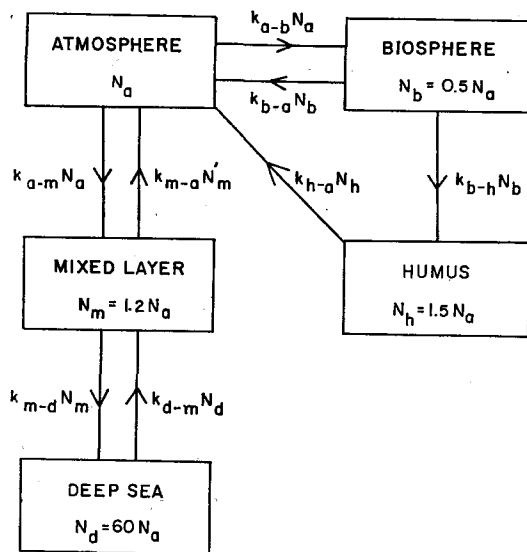
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Fig. 4. Model of the CO_2 exchange between the deep sea, the mixed layer of the sea, the atmosphere, the biosphere and humus on land.

exchange between the atmosphere and the sea takes place. Thus the difference of the C^{14}/C^{12} ratio in the atmosphere and the sea (corrected for fractionation) should be larger in the equilibrium case than in the case where a net transfer occurs as indicated here.

It should be pointed out at this moment that similar deviations of the C^{13}/C^{12} ratios from the equilibrium values may occur if the net transfer of C^{13} and C^{12} are different. This is important since all C^{14} measurements are corrected for fractionation with the aid of the C^{13}/C^{12} ratio. Obviously such a procedure assumes equilibrium conditions. In the case of exchange between the atmosphere and the sea this need not be the case as we have shown above. It so happens, however, that the ratio C^{13}/C^{12} is almost the same in fossil fuel as in the atmosphere, the difference being only about 2 %. Thus no significant errors are therefore introduced in assuming equilibrium conditions.

With the model presented above one can now easily compute how large the deviations from equilibrium are which are due to the fact that a net transfer of both inactive and radioactive carbon occurs. The most likely value of the exchange time again becomes $\tau_{a-m} = 5$ years.

Measurements of C^{14} in the deep sea BROECKER (1957) and RAFTER and FERGUSSON (1958) in many cases indicate an age relative surface

waters of 500 years or more and the interpretation of these values are not essentially influenced by considerations of the kind presented here. It is thus seen from fig. 3 that the computed value of the Süess effect should be around — 5 % in comparison with the observed value of about — 3 %. There may be many explanations for this discrepancy but first of all the accuracy of our model is not greater than it could be explained merely as due to this crudeness. Our assumption of a well-mixed deep sea is of course an unrealistic one and a more complete formulation of the problem in this respect seems very desirable. Secondly, we have completely neglected the effect of the biosphere on land. In view of the relatively small buffering effect of the sea the changes of the CO_2 (as well as $C^{14}O_2$) content of the atmosphere are here computed to be quite large. One may therefore very well expect that the biosphere also is influenced in some way (cf. ERIKSSON and WELANDER, 1956).

5. Estimates of the effect of CO_2 exchange between the atmosphere and the biosphere

The amount of carbon stored in the biosphere on land N_b is not very well known. Different estimates give values varying between 12 % (CRAIG, 1957) and about 85 % (ERIKSSON and WELANDER, 1956) of the amount present in the atmosphere. Estimates of dead organic matter, humus (N_h), also vary considerably, between values of 1.1 N_a to 1.7 N_a. For the following estimates we shall assume $N_b = 0.5 \ N_a$ and $N_h = 1.5 \ N_a$.

We may now extend our previous model of the CO_2-exchange in nature to the one depicted in fig. 4, which in case of equilibrium has been studied by CRAIG (1957). In complete anology with the previous analysis we obtain in the equilibrium case

$$
\left.
\begin{aligned}
-k_{a-m}N_a + k_{m-a}N'_m - k_{a-b}N_a + \\
+ k_{b-a}N_b + k_{h-a}N_a = 0 \\
k_{a-b}N_a - k_{b-a}N_b - k_{b-h}N_b \quad = 0 \\
-k_{h-a}N_h + k_{b-h}N_b \quad = 0 \\
k_{a-m}N_a - k_{m-a}N'_m - k_{m-d}N_m + \\
+ k_{d-m}N_d = 0 \\
k_{m-d}N_d - k_{d-m}N_d \quad = 0
\end{aligned}
\right\} \quad (47)
$$

Again denoting the deviations from equilibrium due to fossil fuel combustion by n_i we obtain

$$\left.\begin{array}{l}\dfrac{dn_a}{dt} + k_{a-m}n_a - k_{m-a}n'_m + k_{a-b}n_a - \\[4pt] \qquad\qquad - k_{b-a}n_b - k_{h-a}n_h = \gamma(t) \\[10pt] \dfrac{dn_b}{dt} - k_{a-b}n_a + k_{b-a}n_b + k_{b-h}n_b \quad = 0 \\[10pt] \dfrac{dn_h}{dt} + k_{h-a}n_h - k_{b-h}n_b \qquad\qquad = 0 \\[10pt] \dfrac{dn_m}{dt} - k_{a-m}n_a + k_{m-a}n'_m + k_{m-d}n_m - \\[4pt] \qquad\qquad\qquad\qquad - k_{d-m}n_d = 0 \\[10pt] \dfrac{dn_d}{dt} - k_{m-d}n_m + k_{d-m}n_d \qquad\quad = 0 \end{array}\right\} \quad (48)$$

It is hardly justified to carry through such a complete analysis here as presented previously in view of the fact that the assumptions made about the exchange processes between the atmosphere, biosphere and humus are more doubtful. An estimate shows, however, that $n_a \approx +7\%$ if we assume $\tau_{a-m} = 5$ years, $\tau_{d-m} = 500$ years, $\tau_{a-b} = 30$ years and $\tau_{b-h} = 30$ years compared with 10% in the case of no net increased assimilation as a result of increased CO_2 content of the atmosphere.

Obviously the distribution of $C^{14}O_2$ between the various reservoirs also is influenced by an exchange with the biosphere and this would be the case even if no net increase of inactive CO_2 in the biosphere and in the humus has occurred. We can obtain a lower limit for the Süess effect if we assume an infinitely rapid adjustment of the C^{14} content between the four reservoirs, the atmosphere, the mixed layer of the sea, the biosphere and humus, i.e. the Suess effect is the same in all reservoirs and also considering that no C^{14} is supplied from the deep sea to these reservoirs. Since $N_m + N_a + N_b + N_h \approx 4\,N_a$ and since the exchange between the mixed layer and the deep sea is comparatively slow so that only a small part $(0.02—0.04\,N_a)$ of the fossil CO_2 released until 1954 $(\approx 0.13\,N_a)$ has found its way into the deep sea we estimate that the Süess effect should be 2—2.5 %. As pointed out previously the observed Süess effect was about -3% in 1954 which is in very good agreement with this estimate.

6. Forecast of the CO_2 changes in the atmosphere during the remainder of the 20th century

Certainly the estimates presented above are partly quite uncertain but it is of some interest
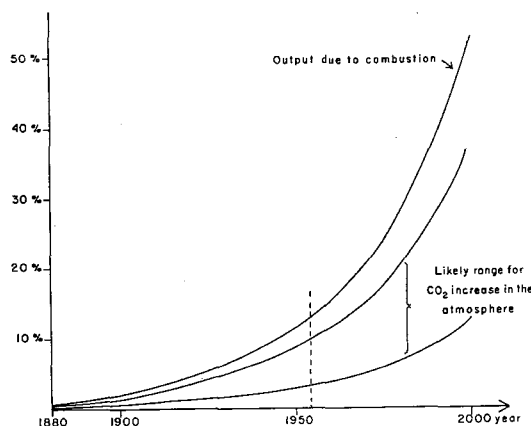

Fig. 5. Estimate of likely range for CO_2 increase in the atmosphere as a result of fossil fuel combustion according to UN estimates.

to see what they imply with regard to future changes of the CO_2-content of the atmosphere. An upper limit is obtained if neglecting the exchange with the biosphere as done in section 4. A lower limit on the other hand is determined if an infinitely rapid exchange between the atmosphere and the biosphere takes place and obviously this would be equivalent to putting N_a equal to the sum of the CO_2 found in the atmosphere, the biosphere and the humus. Introducing the values for the various residence times as given in the previous section yields a forecast in between these two extremes. Fig. 5 shows the variations to be expected until year 2000 based on an output of CO_2 into the atmosphere as given by table 1. The most likely value for n_a at that time seems to be about $+25$ %, it may possibly be larger but probably not exceed 40 %. These values are considerably larger than those estimated for example by REVELLE and SÜESS (1957). The implications with regard to the radiational equilibrium of the earth in such a case may be considerable but falls outside the scope of this paper.

Fig. 5 also shows that the present increase of CO_2 in the atmosphere probably is 0.1—0.3 % per year. Recent measurements in regions far away from industrial areas such as Hawaii and the Antarctica (personal communication from Rakestraw) show remarkably constant values of the CO_2 content in the atmosphere throughout the year. It should therefore be possible within a few years to observe whether an increase occurs with this computed rate or not.

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